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6 **PRIMARY BATTERIES SESSION**
CATALYZED REMOVAL OF
HYDROGEN FROM ELECTRONIC EQUIPMENT,

10 S/Gilman and P/Bramhall
Power Sources Technical Area

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Introduction

The present work was undertaken in order to provide a less expensive and more convenient alternative to the use of a purely mechanical solution to the problem of hydrogen leakage in the Army's AN/PRC-77 Radio Set.¹ The problem originates with hydrogen released by a magnesium battery contained in the battery compartment of the radio. The hydrogen can seep into the electronics compartment if the electrical connector between the two compartments is faulty.

Both the type of problem treated here and the use of a

catalyst for its solution.^{2,4} are not uncommon. For the existing and new-developed catalysts, discussed in this paper, an attempt was made to present performance data in a form more easily translatable to other applications than elsewhere available.

Three types of catalysts were evaluated. One was a "Teflon-bonded" structure which was fabricated in this laboratory using the two methods described in the next section. The second was an "A.D. Little Co. Catalyst" purchased from that company, and the third an "IR-9 Catalyst" provided

from the Federal stockpile by the Naval Mine Engineering Facility, Virginia.

EXPERIMENTAL TECHNIQUES

Measurements of Hydrogen Oxidation Rates

Most experiments were conducted in the modified electronics compartment (Figure 1) by making an initial injection of 300 cm³ of hydrogen (with a hypodermic syringe) into the rubber septum of sample port B and by withdrawing samples of residual hydrogen-air mixtures for chromatographic analysis at ports A or B. The void volume in the electronics compartment was 3400 cm³. Similar experiments were also conducted in a cylindrical aluminum reaction vessel of 960 cm³ volume. A few experiments were conducted under gas flow conditions using a motorized syringe apparatus. An excess of drying agent was present in all experiments to remove product water as formed.

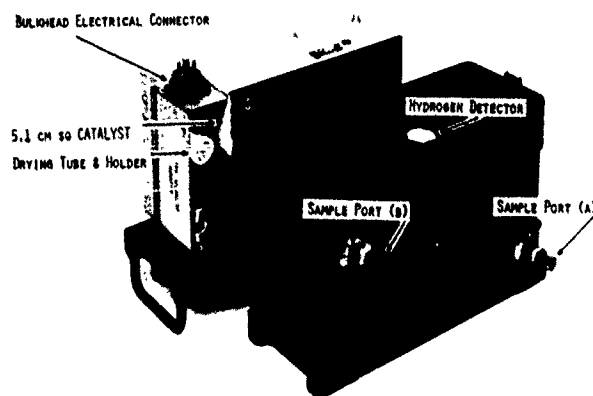


Figure 1. AN/PRC-77 Radio Set Equipped for Gas Analysis.

Preparation of Teflon-Bonded Catalysts

The catalyst developed in this laboratory consists of a carbon-platinum black-Teflon (polytetrafluoroethylene, PTFE) mixture supported on a nickel screen. A porous Teflon membrane is bonded to the side of the catalyst layer facing the reacting gas and serves as a gas diffusion barrier. A 5.1 cm x 5.1 cm square of 0.1 cm thick aluminum is bonded to the reverse side of the catalyst layer and acts as a heat sink. The assembly was accomplished by pressing a 5.1 cm x 5.1 cm nickel screen into a 6.4 cm x 6.4 cm square of Zitex Teflon #HV 100 membrane (0.01 cm thick) using a pressure of 30,000 psi. A mixture of 0.0258 g platinum black (Englehard Co.), 0.38 g Shawinigan carbon black, and Teflon emulsion containing 0.1 g Teflon was blended with 10 cm³ of water and the mixture applied to the nickel screen by means of a spatula. The assembly was pressed at 12,000 psi, air dried, and then vacuum dried at 115°C. The assembly was then trimmed to 5.1 cm x 5.1 cm and then, with the Zitex membrane up, was cemented to the aluminum square using G.E. silicone rubber.

A similar catalyst unit was assembled starting with an American Cyanamid (fuel cell) air cathode having a platinum loading of 1 mg/cm² with carbon as the diluent. The air

cathode already incorporated the required porous Teflon and Teflon-bonded Teflon/carbon layers.

RESULTS AND DISCUSSION

Catalyst Performance Requirements

For the purpose of defining catalyst requirements, the space to be protected against hydrogen build-up may be considered a baffled 3400 cm³ volume, sealed off from the external atmosphere, with an inflow of up to 200 cm³ of hydrogen per day (estimated worst case). It is required that the catalyst be capable of combining 200 cm³ of hydrogen per day while maintaining the hydrogen concentration below 4.1% ("lower limit of flammability") and for oxygen concentrations as low as 4.4% (mixtures containing less oxygen are non-flammable). Further, the requirement holds for temperatures at least as low as -5°C with performance at even lower temperatures desirable.

Since no re-entry of air is stipulated above, reaction of hydrogen with the atmospheric oxygen originally enclosed would eventually lead to a nitrogen-hydrogen mixture which would be further enriched in hydrogen by diffusional interaction with pure hydrogen from the battery. The final enclosed volume of pure hydrogen could be ignited only if the system is opened to the external atmosphere (e.g., unintentionally due to mechanical failure, or intentionally during a servicing operation). This consideration helps lead to the final requirement that the catalyst not be capable of igniting any hydrogen-air mixture under any condition of mixing and for temperatures up to 71°C. Further, the catalyst must not suffer any thermal self-destruction or degradation under extreme reaction conditions. This places an upper limit on the acceptable reactivity of the catalyst.

A. D. Little Company Catalyst System

The units^{6,7} obtained for evaluation were developed for the more hazardous (pure oxygen-hydrogen mixtures and pressures above one atmosphere) conditions encountered in a sealed rechargeable battery overcharging at the one-ampere rate. They tend, therefore, to be more conservatively designed than required for the present application. The units evaluated consisted of 4 ceramic pellets, containing small amounts of a noble metal, housed in a glass tube (2.5 cm I.D. X 3.8 cm long) with porous Teflon end-plates. Figure 2 plots the variation of hydrogen concentration for a catalyst-equipped radio set after initial injection of 300 cm³ of hydrogen. The linear semilogarithmic plots of Figure 2 imply the following relationship:

$$-d \ln p/dt = k_t \quad (1)$$

where p is the partial pressure of hydrogen and k_t is the slope of the line. Relationship (1) implies, in turn:

$$-dp/dt = k_t p \quad (2)$$

The quantity $-dp/dt$ is a rate of hydrogen oxidation and k_t is an "apparent specific rate" for the particular configuration of catalyst, container volume, and for the temperature, t . Values of k_t , for this and the other catalysts discussed in this paper, appear in Figure 3.

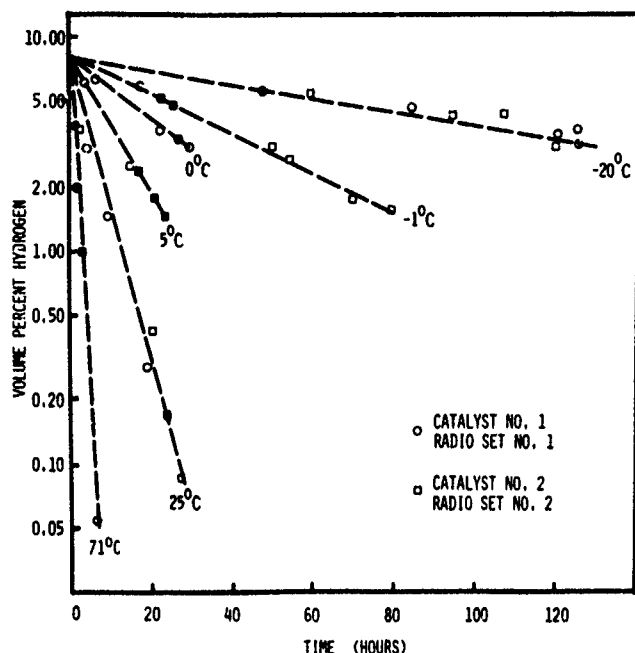


Figure 2. Hydrogen Concentration in the Electronics Compartment of an AN/PRC-77 Radio Set Equipped with a 1-Ampere Size A. D. Little Catalyst; Hydrogen Injected into Set.

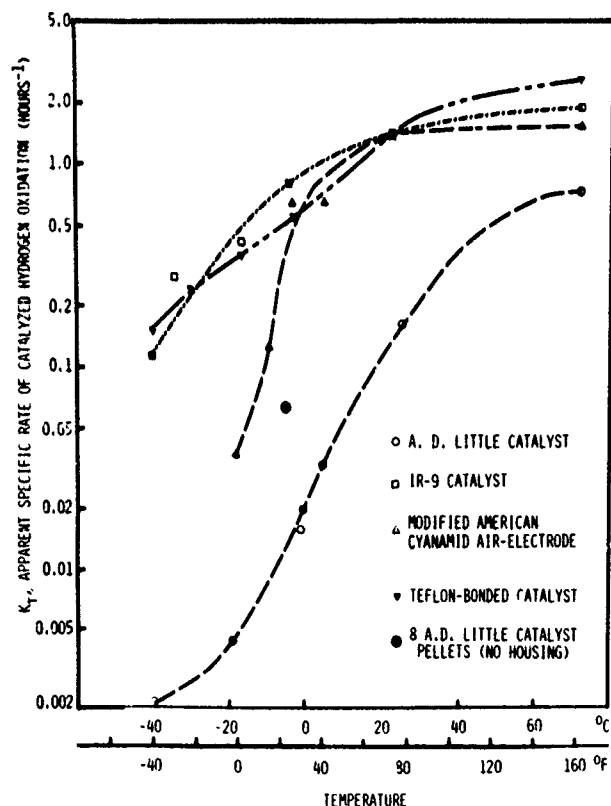


Figure 3. Apparent Specific Hydrogen Oxidation Rates (k_t) for Several Different Catalysts as Determined for a 3400 cm^3 Reaction Volume.

Although Equation (2) suggests the type of "first order reaction kinetics" reported for some pure metal catalysts of simple geometry it actually reflects complicated transport barriers to the reactant hydrogen, rather than inherent

chemical reactivity. This is evidenced by the inability to obtain a good Arrhenius plot for the values of k_t and by the steepness of such a plot in the vicinity of the freezing point of water. Diffusional hindrances in the ADL catalyst occur at the porous Teflon outer membrane and within the porous structure of the ceramic pellet. For the experiments of Figure 2, no corresponding oxygen transport influence is evident or expected since oxygen remains in relative excess during the entire course of the experiment.

The observed temperature dependence of k_t (Figure 3) suggests that condensed product water or ice makes important contributions to the diffusional hindrances.

Removal of the outer porous Teflon barrier results in a 64% rate increase in k_t at room temperature. Furthermore, as anticipated, rates were found to be roughly proportional to the number of ceramic catalyst pellets and inversely proportional to the volume of the reaction vessel. The rate, at -5°C , for eight (8) "unhoused" pellets is recorded on Figure 3.

Using Equation (2), the minimum requirement of a 200 cc/day hydrogen oxidation rate at a maximum 4.1% hydrogen concentration may be expressed in terms of a minimum value of k_t . That value is 0.06 hour^{-1} and is attainable down to -5°C for the ADL catalyst if 8 "unhoused" pellets are utilized.

While the initial rapid injection of a fixed volume of hydrogen was selected as the most convenient method for evaluating catalysts, actual conditions for the application at hand most nearly approximate a steady flow of hydrogen into the test chamber. For such a condition, Equation (2) suggests that a "quasi-steady state" partial pressure or concentration of hydrogen will be established eventually and will then be maintained until oxygen is seriously depleted. Figure 4 shows the result of an actual steady-flow experiment with a complete ADL catalyst unit and 160 cm^3/day inflow rate.

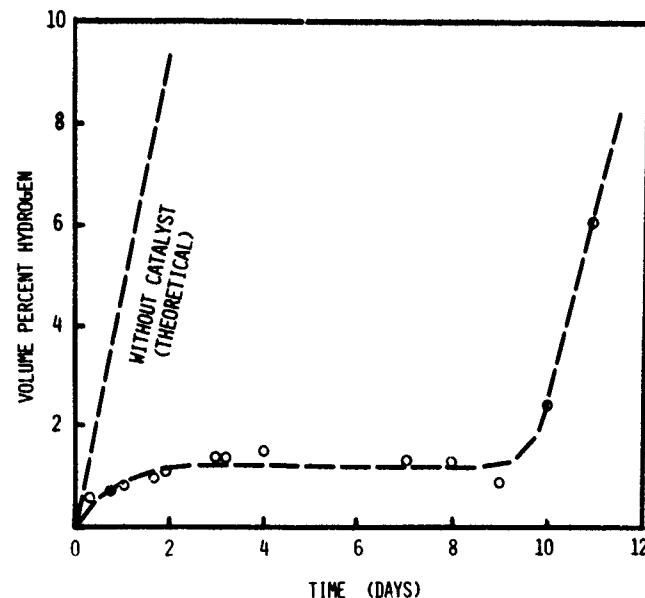


Figure 4. Hydrogen Concentration in the Electronics Compartment of an AN/PRC-77 Radio Set Equipped with an A. D. Little Catalyst and with a Steady Inflow of Hydrogen.

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The plateau value of the hydrogen concentration is 1.2% in good agreement with calculation based on the value of k_t taken from Figure 3.

Teflon Bonded and "IR-9" Catalysts

The results for the Teflon-Bonded Catalyst, appearing in Figure 5, were obtained as already described for the ADL catalyst. The semilogarithmic plot is not linear initially possibly since the initial high rates and self-heating delay the establishment of steady mass transport conditions. The slopes, k_t , of the later (more linear) portions of the plots are plotted in Figure 3. Results were similarly obtained for a Teflon-bonded structure fabricated from an American Cyanamid air electrode and for an "IR-9 Catalyst." The latter catalyst system has been useful for Naval^{3,8} applications and was originally developed by the Industrial Research Corporation (with the trade name "Hydrocaps") for use with lead-acid batteries. The active components of the IR-9 are a number of Pd-coated 0.32 cm x 0.32 cm pellets which are packed in a chemical powder and a metal housing/heat sink.

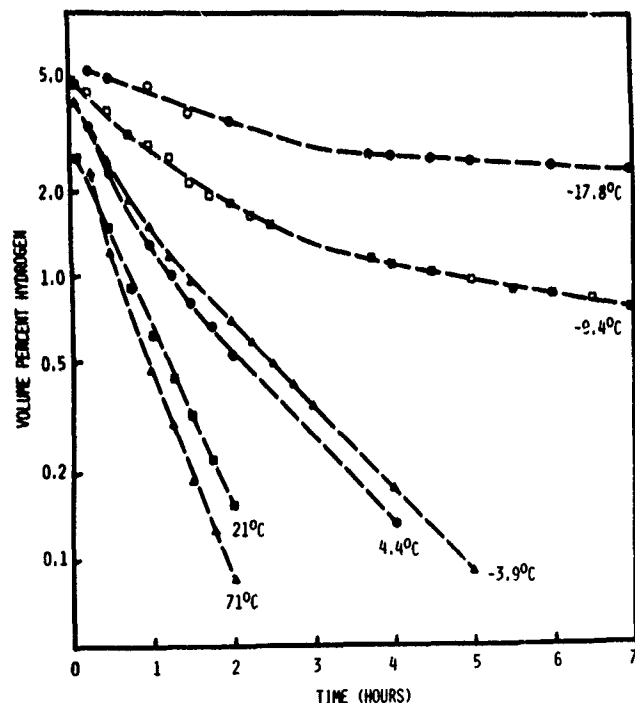


Figure 5. Hydrogen Concentration in the Electronics Compartment of an AN/PRC-77 Radio Set Equipped with a Teflon-Bonded Catalyst Made in this Laboratory, Hydrogen Injected into Set.

Safety Evaluation of Catalysts

Catalysts were evaluated by dropping into a pre-mixed 30% hydrogen-air mixture using a specially designed apparatus. None of the catalysts covered in Figure 3 caused detonation or underwent obvious thermal degradation.

Under the same conditions, pure Pt and Pd black caused explosions and an unmodified American Cyanamid electrode was found to shrivel and de-laminate.

Hydrogen Detector

A simple hydrogen detector was constructed (placement shown in Figure 1) using a small piece of the Teflon-bonded catalyst material (less the heat sink) discussed previously. A piece of cobalt chloride saturated paper in contact with the catalyst absorbed product water and provided a blue-to-pink color transition when a burst of hydrogen was introduced into the set whether or not a larger internal catalyst was present. The detector communicated with the internal atmosphere by means of a small tapped hole already present in the bottom of the chassis box.

Conclusion

The rates appearing on Figure 3 apply for catalysts of specific and rather arbitrary size (S) and for a 3400 cm³ reaction volume (V). For any other circumstances, rates should be proportional to S/V, barring unforeseen heat and mass transfer complications. For the particular application at hand, and the requirement that k_t be greater than 0.061 hour⁻¹, the 8 "unhoused" A. D. Little pellets and the other types of catalysts listed would suffice for the catalyst sizes selected here. However, since all of the catalysts can be sized upwards (for greater efficiency) or downwards (for economy), they are best compared on the basis of their cost and bulkiness for the same level of reactivity. Of the three types of catalysts under consideration, the Teflon-bonded is by far the least bulky, tending least to obscure componentry and leaving the most open volume for drying agent. That structure in the size selected for evaluation here is expected to cost approximately as much as the IR-9 catalyst and a fraction of the price of eight (8) ADL catalyst pellets.

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